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4-Phenyl-1,2,4-triazoline-3,5-dione in the ene reactions with cyclohexene, 1-hexene and 2,3-dimethyl-2-butene. the heat of reaction and the influence of temperature and pressure on the reaction rate

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Abstract

The values of the enthalpy (53.3; 51.3; 20.0 kJ mol-1), entropy (-106; -122; -144 J mol-1K-1), and volume of activation (-29.1; -31.0; -cm3 mol-1), the reaction volume (-25.0; -26.6; -cm3 mol-1) and reaction enthalpy (-155.9; -158.2; -150.2 kJ mol-1) have been obtained for the first time for the ene reactions of 4-phenyl-1,2,4-triazoline-3,5-dione 1, with cyclohexene 4, 1-hexene 6, and with 2,3-dimethyl-2-butene 8, respectively. The ratio of the values of the activation volume to the reaction volume (ΠV≠ corr/ΔVr - n) in the ene reactions under study, 1 + 4→5 and 1 + 6→7, appeared to be the same, namely 1.16. The large negative values of the entropy and the volume of activation of studied reactions 1 + 4→ 5 and 1 + 6→7 better correspond to the cyclic structure of the activated complex at the stage determining the reaction rate. The equilibrium constants of these ene reactions can be estimated as exceeding 1018 L mol-1, and these reactions can be considered irreversible. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords

1-hexene, 2,3-dimethylbytene-2, 4-phenyl-1,2,4-triazolin-3,5-dione, activation volume, cyclohexene, ene-reaction, enthalpy reaction, high pressure effect, rate constant